

Mechanism for the ablation of Si(111) with pairs of ultrashort laser pulses

Zhan Hu

Institute of Atomic and Molecular Physics, Jilin University, Changchun, People's Republic of China 130021

Sima Singha, Yaoming Liu, and Robert J. Gordon^{a)}

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607-7061

(Received 3 November 2006; accepted 21 February 2007; published online 28 March 2007)

Pairs of ultrafast laser pulses are used to ablate Si(111). The fluorescence from Si atoms and ions was observed to increase by an order of magnitude as the delay between the pulses was increased. From the dependence of the fluorescence enhancement on the laser fluence and the pulse delay, it is deduced that the first pulse melts the surface and that the second pulse interacts more strongly with the liquid phase. © 2007 American Institute of Physics. [DOI: 10.1063/1.2716838]

Laser ablation of materials is a complex phenomenon involving several phases and multiple length and time scales.¹ Ultrafast (sub-100-fs) pulses are a powerful tool both for probing and controlling the ablation mechanism.² For example, Stoian *et al.*³ and Spyridaki *et al.*⁴ used trains of ultrafast pulses to modify the morphology of the ablation crater. Subsequently, Dachraoui and Husinsky⁵ showed that by shaping the pulse train using a genetic algorithm, it is possible to enhance the amount of Si ions emitted from the surface. In another study, Koudoumas *et al.*⁶ measured the kinetic energies of Si ions produced by a pair of short pulses. From the dependence of the yields and energies of the ions on the delay between the pulses, they proposed that the first pulse melts the crystal surface and that the second pulse ablates the liquid phase.

Here we examine the two-pulse mechanism more closely, using atomic and ionic fluorescence and atomic force microscopy (AFM) as our primary observables. The apparatus consists of an ultrafast laser, a Michelson interferometer to generate double pulses with a controllable delay, a sample manipulator, and an optical detector. The radiation source is a regeneratively amplified Ti:sapphire laser (Spectra Physics Tsunami oscillator and Spitfire amplifier), which delivers 800 nm, 45 fs pulses with a maximum pulse energy of 2 mJ at a 1 kHz repetition rate. Care is taken to ensure that the energies of two pulses (referred to as “half pulses”) are equal. The combined energy of the two half pulses reaching the sample range from 0.6 to 11.5 μJ . Single-pulse experiments are performed by blocking one of the beams.

Undoped Si(111) wafers (MTI Crystal, 0.5 mm thick) are used as received from the manufacturer. The sample is mounted in air on a motorized XYZ stage, which rasters it to a new location after each laser shot. The sample is positioned with its normal axis at an angle of 30° with respect to the laser beam direction. The *s*-polarized laser beam is focused onto the sample by an objective lens with a numerical aperture of 0.25 to a spot size of 3.6 μm in diameter. Fluorescence perpendicular to the laser beam is collected by an *f*/2.0 lens, focused into a 0.25 m monochromator, and detected with a photomultiplier tube (Hamamatsu R928). The shape of the ablated surface is measured by AFM (Veeco Nanoscope III SPM).

The principle experimental result is shown in Fig. 1. Fluorescence from neutral atomic Si at 288.2 nm ($^1D_2\text{-}^1P_1$) is measured as a function of the delay t between the two laser pulses, with a combined fluence F ranging from 6 to 105 J/cm². The fluorescence signal is found to increase monotonically with t , as illustrated in Fig. 1(a). Fitting of the signal to the functional form $A(1-e^{-|t|/\tau})$ gives a time constant of $\tau=40\text{--}50$ ps, which varies weakly with F . Measurements of Si II fluorescence at 505.6 nm give quantitatively similar results. The enhancement ratio, $E(F, t)$, defined as the ratio of the fluorescence signal for the pulse pair to that for a single pulse having the same total F , is plotted in Fig. 1(b) as a function of t and F . The highest enhancement ratio is 20.7, obtained at $t=104.8$ ps and $F=6.1$ J/cm². Figure 1(b) shows that $E(F, t)$ always increases with $|t|$ for a fixed F , but that at a fixed delay the enhancement decreases with fluence.

AFM measurements are performed to determine the volume and shape of the ablated craters. In single-pulse experiments we find that the volume of the crater is approximately proportional to the laser fluence. The fluorescence signal also varies smoothly with fluence, and, therefore, as shown by the solid points in Fig. 2, the fluorescence signal varies linearly with the ablated volume at low fluence.⁷ For double pulses, however, the crater morphology and fluence dependence of the fluorescence are more complex. The open points in Fig. 2 show that at fixed fluence the crater volume is roughly independent of pulse delay, even though the fluorescence increases with delay. In another experiment (not shown), we record the AFM images of craters that were etched for one hour with 44% KOH solution. Utilizing the property that KOH etches Si(111) much more slowly than amorphous Si,^{8,9} we determine that the craters produced by double pulses contain a large amount of resolidified material that increases with t .

The AFM data show that both half pulses reach the surface and ablate it. The question is what produces the enhancement effect, and what is the physical meaning of the time constant τ . If the only effect of the laser radiation is to excite and vaporize some of the surface molecules, and if the fluence of each pulse exceeds the threshold for ablation (as is the case here), one would expect an additive response, such that $E(F, t)=1$. Evidently, the first pulse induces a structural change of some sort, enabling the second pulse to couple more strongly with the modified material. There are two pos-

^{a)}Electronic mail: rjgordon@uic.edu

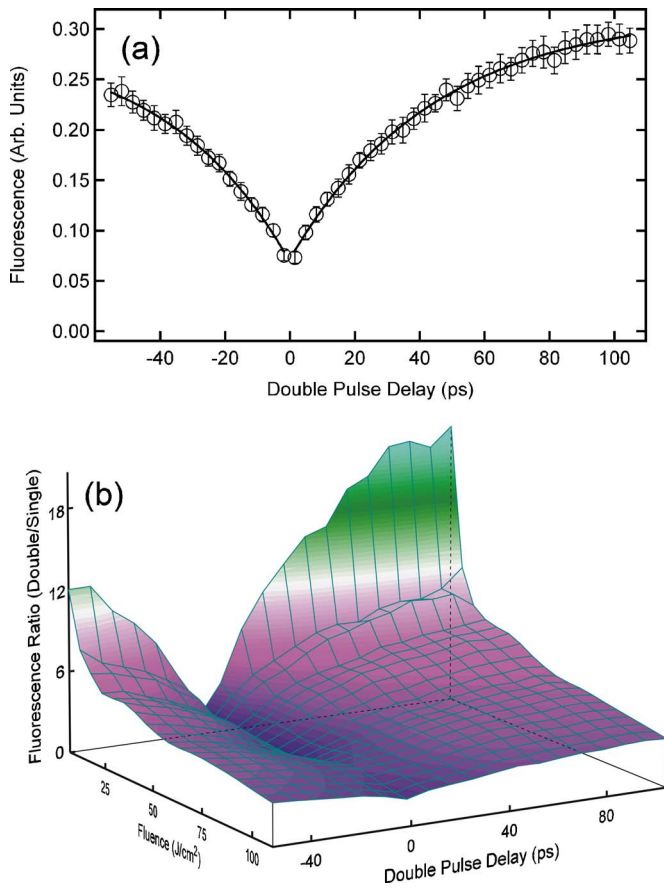


FIG. 1. Atomic fluorescence produced by the double pulse ablation of Si(111). (a) Fluorescence vs delay time at a combined fluence of 48.7 J/cm^2 . Each point is the average of 40 pulses, with each pulse ablating a fresh surface area. The error bars are a single standard deviation. The smooth curve is a least squares fit of an exponential function. (b) Enhancement ratio as a function of delay time and fluence. The three-dimensional representation is based on delay scans taken at seven different fluences.

sible mechanisms (although a combination of both is also possible). In the first mechanism (mechanism I), the first pulse melts the surface and the second pulse interacts more strongly with the liquid, as proposed by Koudoumas *et al.*⁶ The second possibility (mechanism II) is that the enhanced fluorescence is produced by multiphoton excitation of atoms and particles in the plume produced by the first half pulse, as proposed by Semerok and Dutouquet¹⁰ for Cu ablation.

We may distinguish between these mechanisms by considering the fluence dependence of $E(F, t)$. Simply put, for mechanism II we expect the enhancement to increase with fluence as the concentration of particles in the plume increases with F , whereas in mechanism I we expect $E(F, t)$ to decrease with F because of shielding by the plume. This reasoning is made more precise by the following analysis.

The number of fluorescence photons produced by the single large pulse is given by

$$N_1 = \frac{F}{h\nu} A q_s, \quad (1)$$

where $h\nu$ is the laser photon energy, A is the effective area of the focal spot, and q_s is the average conversion efficiency of laser photons into fluorescence photons. Similarly, the number of photons generated by the pulse pair is given by

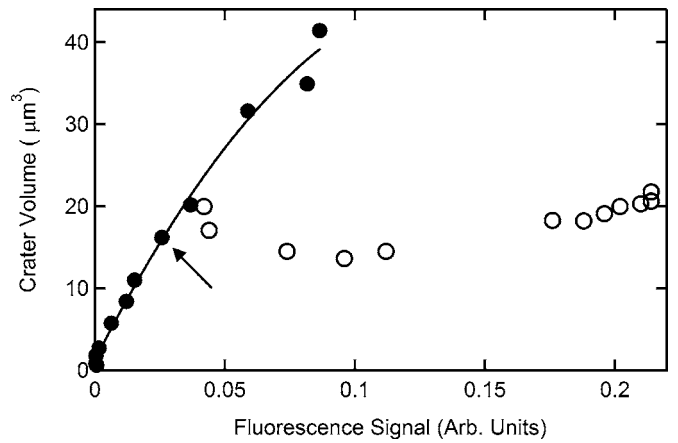


FIG. 2. Atomic force microscopy measurements of Si crater volume vs fluorescence intensity for single (solid points) and double (open points) pulses. The solid points are for craters produced with different fluences, ranging from 6.2 to 91.4 J/cm^2 . The open points are produced at a constant fluence of 41.5 J/cm^2 , with the delay ranging from 0 to 105 ps . The arrow indicates a single pulse measurement performed at the same fluence used for all the double pulse measurements. The solid line is drawn to guide the eye.

$$N_2 = \frac{F}{2h\nu} A [q_s + f_p(F, t)q_p + g_l(F, t)q_l + g_{s'}(F, t)q_{s'}], \quad (2)$$

where the first term in the brackets gives the number of fluorescence photons produced by the first half pulse, and the second through fourth terms denote the number of photons generated by the second half pulse in the plume, liquid phase, and solid phase (beneath the liquid front), respectively. In Eq. (2), q_p , q_l , and $q_{s'}$ are the average conversion efficiencies of the second pulse in the plume, liquid, and solid phases, respectively. The quantity $f_p(F, t)$ is the fraction of the second half pulse absorbed by the plume. The quantity $g_l(F, t)$ is given by

$$g_l(F, t) = (1 - f_p(F, t))f_l(F, t), \quad (3)$$

where f_l is the fraction of light absorbed by the liquid phase for $f_p(F) < 1$, and zero otherwise. Similarly,

$$g_{s'}(F, t) = 1 - g_l(F, t) \quad (4)$$

for $g_l(F, t) < 1$, and zero otherwise. Making the reasonable assumption that q_s has the same value in Eqs. (1) and (2) (i.e., that it depends weakly on the fluence), we can write the enhancement ratio as

$$E(F, t) = N_2/N_1 = \frac{1}{2} \left[1 + f_p \frac{q_p}{q_s} + g_l \frac{q_l}{q_s} + g_{s'} \frac{q_{s'}}{q_s} \right]. \quad (5)$$

In the high fluence and long time limit, where the second pulse is absorbed entirely by the plume and liquid, the last term in Eq. (5) vanishes. It follows that the condition for $E \gg 1$ is $f_p(q_p/q_s) + g_l(q_l/q_s) \gg 1$. We consider the following two limiting cases:

- (a) $f_p(q_p/q_s) \ll 1$ and $g_l(q_l/q_s) \gg 1$
- (b) $f_p(q_p/q_s) \gg 1$ and $g_l(q_l/q_s) \ll 1$.

Case (a) corresponds to the enhancement produced mostly in the liquid phase (mechanism I) and case (b) corresponds to the enhancement produced in the plume (mechanism II). We may distinguish between these two cases experimentally by examining the fluence dependence of

$E(F, t)$. As the fluence increases, a larger fraction of the second pulse is absorbed by the plume. In case (a), $q_p/q_s \ll 1$, $q_l/q_s \gg 1$, and the enhancement ratio decreases with fluence to a limiting value of $\frac{1}{2}$, as $f_p \rightarrow 1$ and $g_l \rightarrow 0$. In case (b), $q_p/q_s \gg 1$ and the enhancement ratio increases with fluence to a limiting value of $\frac{1}{2}[1 + (q_p/q_s)]$, as more plume particles fluoresce. Experimentally we observe for Si that E decreases with F , corresponding to case (a). Enhanced fluorescence originating in the plume has been observed for Si(111), but only at much higher fluences (100–1000 J/cm²) and with enhancement ratios one to two orders smaller than observed here.¹¹

The mechanism that emerges from this analysis is as follows. The first pulse superheats the Si surface¹² and melts it electronically. Some of the atoms absorb enough photons to produce electronically excited Si and Si⁺, which fluoresce. Ablation craters are also formed, with volumes given by the solid points in Fig. 2. Some of the absorbed energy is retained by the liquid, creating a phase boundary that propagates inward at roughly the speed of sound.¹³ The second pulse couples more strongly to the liquid phase, producing a larger fraction of electronically excited Si and Si⁺, causing the enhanced fluorescence. The rise time of $E(F, t)$ is given approximately by the penetration depth in the liquid divided by the speed of sound.¹ The AFM images of the etched craters show that the double pulse enhances the amount of material transformed. We posit that some of the material ablated by the second pulse condenses back into the crater after colliding with the plume produced by the first pulse. Evidence of interaction of the two plumes is seen in published shadowgraph images.¹⁴ We also speculate that the plume produced by the first pulse partially shields the surface from the second pulse, causing $E(F, t)$ to decrease with increasing F at fixed t .

In conclusion, we have shown that atomic and ionic fluorescence are a good measure of the damage done to a surface by an ultrafast laser. Splitting the pulse into two half

pulses enhances the fluorescence by an amount that increases with delay and decreases with fluence. From its fluence dependence we deduce that the enhancement is caused by the first pulse melting the surface and the second pulse interacting more strongly with the liquid phase.

The authors are grateful to Yehiam Prior and David Seidman for fruitful discussions. They wish to thank the National Science Foundation for its generous support under Grants Nos. PHY-0200812, CHE-0120997, and CHE-0640306, as well as the Motorola Physical Realization Research Center in Schaumburg, IL, for cosponsoring this research. Support by the National Science Foundation of China under Grant No. 10404008 is acknowledged by one of the authors (Z.H.).

¹B. Rethfeld, K. Sokolowski-Tinten, D. Von Der Linde, and S. I. Anisimov, Appl. Phys. A: Mater. Sci. Process. **79**, 767 (2004).

²A. Rouse, C. Rischel, S. Fourmaux, I. Uschmann, S. Sebba, G. Grillon, Ph. Balcou, E. Forster, J. P. Geindre, P. Audebert, J. C. Gauthier, and D. Hulin, Nature (London) **410**, 65 (2001).

³R. Stoian, M. Boyle, A. Thoss, A. Rosenfeld, G. Korn, I. V. Hertel, and E. E. B. Campbell, Appl. Phys. Lett. **80**, 353 (2002).

⁴M. Spyridaki, E. Koudoumas, P. Tzanetakis, C. Fotakis, R. Stoian, A. Rosenfeld, and I. V. Hertel, Appl. Phys. Lett. **83**, 1474 (2003).

⁵H. Dachraoui and W. Husinsky, Phys. Rev. Lett. **97**, 107601 (2006).

⁶E. Koudoumas, M. Spyridaki, R. Stoian, A. Rosenfeld, P. Tzanetakis, I. V. Hertel, and C. Fotakis, Thin Solid Films **453–454**, 372 (2004).

⁷Y. Prior, K. Zhang, V. Batenkov, Y. Paskover, J.-H. Klein-Wiele, and P. Simon, Proc. SPIE **5448**, 1049 (2004).

⁸D. L. Kendall, Annu. Rev. Mater. Sci. **9**, 373 (1979).

⁹H. Fuhrmann, M. Dobeli, R. Muhle, and M. Suter, J. Vac. Sci. Technol. B **17**, 945 (1999).

¹⁰A. Semerok and C. Dutouquet, Thin Solid Films **453–454**, 501 (2004).

¹¹P. P. Pronko, Z. Zhang, and P. A. VanRompay, Appl. Surf. Sci. **208–209**, 492 (2003).

¹²P. Lorazo, L. J. Lewis, and M. Meunier, Phys. Rev. B **73**, 134108 (2006).

¹³B. Rethfeld, K. Sokolowski-Tinten, D. von der Linde, and S. I. Anisimov, Phys. Rev. B **65**, 092103 (2002).

¹⁴T. Y. Choi, D. J. Hwang, and C. P. Grigoropoulos, Appl. Surf. Sci. **197–198**, 720 (2002).